REACTION BEHAVIORS OF MIXED PLASTICS IN LIQUID-PHASE CRACKING

Jyi-Perng A. Wann, Tohru Kamo, Hiroshi Yamaguchi*, and Yoshiki Sato
National Institute for Resources and Environment, Tsukuba, Ibaraki; 305 Japan
*Engineering Research Center, NKK Corp., Kawasaki, Kanagawa, 210 Japan

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INTRODUCTION

The majority of waste plastics today is either incinerated or buried for landfills. However, incineration of waste plastics can cause damages in furnace and air pollution problems. Shortage of available landfill sites also has become a serious concern. The methods of waste plastic recycling therefore have been paid much attention with the viewpoint of effective environmental protection. Liquefaction of waste plastics is an attractive recycling method in terms of producing fuel oil or chemicals. To date, most of the waste plastic liquefaction investigations have been limited to the areas not involving the use of a solvent. Pilot-scaled plants, such as those in the Fuji Recycle Process in Japan [1] and the VCC Process in Germany [2], have been operated for some time. Although high conversion of waste plastics can be obtained at a temperature as low as 400 °C, problems such as wide molecular weight distribution in the produced oil and high coking tendency have been encountered. Liquid-phase cracking of waste plastics has the potential of overcoming these problems, yet few research has been reported on the liquefaction behaviors for the liquid-phase cracking [3-5]. Polyethylene (PE) has been regarded as one of the polymers difficult to liquefy, while the cracking of polystyrene (PS) is considered to proceed in a way different from that of PE. Hence, we investigated the cracking of PS, PE, and their mixtures using solvents of different hydrogen donation capability. Differences in the liquefaction behaviors between PS and PE, influences of the solvent type, synergistic effects for the liquefaction of PS/PE mixtures, and a property in the oil are presented in this paper.

EXPERIMENTAL

Pellet-sized high-density PE (Mitsui Petrochemical Co.) and PS (Dai-Nippon Ink Chemicals) of commercial grades were used. Reagent-grade tetralin (>97% purity) and n-decane (>99% purity) (Tokyo Chemical Industry Co.) were used without further purification. A total weight of 80 g of the plastic-solvent mixture was charged into a 300-mL autoclave reactor in each run. The wt./wt. ratio between the plastic and the solvent was 1/3 or 1/0. For the liquefaction of plastic mixtures, the wt./wt. ratio of PS to PE used was 3/1, 1/1, or 1/3. The reactor was charged with nitrogen to 40 kg/cm^2 (570 psig) at room temperature. The reaction was conducted at 440 °C for 60 min, with constant stirring at 1000 rpm. The volume and the composition of the produced gases were measured after reaction. The produced liquid, of which the weight was calculated based on the assumption of no weight loss for light products at room temperature, was distilled under a vacuum less than 1 torr. The recovered liquid, with the boiling point range lower than 538 °C, was further analyzed with a GC–FID system equipped with a capillary column. The oil yield was calculated with the following equation:

$$\text{Oil yield, (wt./wt. basis)} = \frac{\text{wt. (recovered liquid)} - \text{wt. (charged solvent)}}{\text{wt. (charged plastic)}}$$

Concentrations of, mainly, benzene, toluene, and some alkylbenzenes and n-alkanes, were measured by the FID-GC analysis.

RESULTS AND DISCUSSION

Cracking of PS

The yields of products from PS cracking at 440 °C, with and without solvent addition, are presented in Table 1. The results for corresponding solvent blank runs are also included for comparison. In the absence of a solvent, the yields of gas, oil, and residue were 0.3, 72.9, and 26.8%, respectively. Toluene, ethylbenzene, and cumene were the main liquid products from PS. Benzene, styrene, and n-propylbenzene were produced in relatively low quantities. We found that a much higher molar quantity of toluene was produced than that of methane. This suggests that the majority of the toluene may not come directly from the cracking of ethylbenzene.

When n-decane was used, the yields of gas, oil, and residue were 5.1, 83.8, and 11.1%, respectively. Under the reaction condition, n-decane was expected to be an inert solvent, because only a small amount of n-alkanes in C5–C9 range was produced during the n-decane solvent blank run. Nevertheless, a slight increase in the total yield of gas, which includes ethane, propane, and n-butane that can be converted from n-decane, has been observed in the reaction with PS. The increased gas yield indicates that the presence of PS may have enhanced the decomposition of n-decane slightly. The higher oil yield, when compared to the case without the solvent addition, suggests that the occurrence of condensation reactions may be decreased by a dilution effect from n-decane solvent.

The highest oil yield of 95.8% was obtained when tetralin was the solvent. This could be due to both the effects of solvent dilution and hydrogen donation from tetralin solvent.

<u>Cracking of PE</u>

Table 2 shows the distribution of products from PE cracking at 440 °C. Without the solvent addition, the yields of gas, oil, and residue were 1.7, 53.9, and 44.4%, respectively. The characteristic distribution of n-alkanes in the produced oil indicates that the decomposition of PE proceed by radical chain reactions [1]. Very low oil yields of 1.6% and 0.8% were obtained for the cracking in n-decane and in tetralin, respectively. The decreased conversion of PE with n-decane may be due to a retardation effect resulting from solvent dilution to the induced cracking of PE. The lowest conversion of PE, obtained in tetralin, suggests that the combined effects of dilution and hydrogenation by tetralin may have further retarded the decomposition of PE.

<u>Cracking of PS/PE Mixtures</u>

<u>No solvent addition.</u> Figure 1 shows the yields of toluene, ethylbenzene, cumene, n-alkanes in C5–C9 range, and oil yield in the reaction without solvent addition. At each PE fraction (as expressed by PE/(PE+PS) in Figures 1–3) of 0.25, 0.50, and 0.75, the oil yield of the plastic mixtures was higher than that of each comprising plastic. The fairly constant yield of toluene and the slight decreased yield of ethylbenzene, as observed for the PE fractions from 0 to 0.50, suggests that cracking of PS may have been enhanced by the mixing from PE. The total yield of n-alkanes in C5–C9 range produced from PE was low but increased proportionally with the increasing amount of PE in the feed mixtures. This indicates that the presence of PS did not enhance the cracking of PE. Therefore, it is considered that the enhanced conversion of PS to oil could be mainly due to a dilution effect resulted from PE, similar to that from n-decane to the cracking of PS, as discussed earlier.

<u>n-Decane as the solvent.</u> Figure 2 shows the effect of n-decane on the distribution of products due to PE and PS mixing. The figure shows significant synergistic effects for oil yields in the mixtures. The yields of toluene, ethylbenzene, and cumene decrease almost linearly with the increased PE fraction in the feed mixtures. The trend for the products implies that cracking of PS may not be significantly enhanced by the presence of PE. The high synergistic effect for oil yield at the PE fraction of 0.75 could be mainly due to the enhanced contribution from PE cracking since the dilution effect from the solvent may be considered equal for all the fractions. The yield of C5–C9 n-alkanes was fairly constant in the PE fraction ranges from 0 to 0.75. This indicates that the n-alkanes may be produced from the decomposition of n-decane, PE, or the both.

<u>Tetralin as the solvent.</u> Figure 3 shows the effect of tetralin on the distribution of products due to PE and PS mixing. The yields of oil and each light aromatic compound from PS decreased monotonously with the increased PE fraction. The results also show that the effects of tetralin for oil yield increases in the mixtures were not as pronounced as in the aforementioned two cases. The nearly linear relationship between the yields of each products at each PE fraction indicates that the synergistic effects between PS and PE could be low in tetralin solvent. It may be a result of rapid stabilization by hydrogen donation from tetralin to the radicals produced from PS cracking.

CONCLUSIONS

The use of solvents can play important roles in the liquefaction of plastics. For the liquid-phase cracking of PS, it has been demonstrated that the oil yield can be increased by the minimization of condensation reactions. On the other hand, the oil yield for PE cracking can be decreased as a result of retardation to radical chain reactions, due to the dilution or hydrogen donation effect from the solvents. Interactions between PS and PE also can be influenced by the solvents used. Liquid-phase cracking shows a promising direction for the processing of waste plastics by proper selection of reaction systems.

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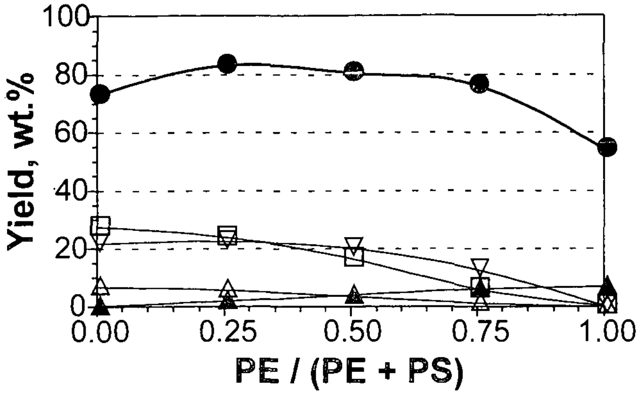
Table 1. Yields of products from blank runs and from PS cracking at 440 °C

Reaction Environment:	**Tetralin**		**n-Decane**		**No Solvent**
wt.% of PS	**Blank[1)]**	**440 °C**	**Blank[1)]**	**440 °C**	**440 °C**
Gas	**0.0**	**0.7**	**2.1**	**5.1**	**0.3**
Oil		**95.8**		**83.8**	**72.9**
benzene	0.0	0.2	0.0	0.7	0.9
toluene	0.2	40.8	0.0	33.3	21.6
ethylbenzene	0.2	27.7	0.0	13.4	27.4
styrene	0.0	0.5	0.0	0.5	0.0
cumene	0.0	5.5	0.0	3.7	6.6
n-propylbenzene	0.0	1.5	0.0	1.6	1.3
total light aromatics	0.4	76.2	0.0	53.1	57.8
total C5–C9 n-alkanes	0.0	0.0	7.8	1.0	0.1
Residue		**3.5**		**11.1**	**26.8**

Note:1) data calculated on the basis of the initial weight of plastic

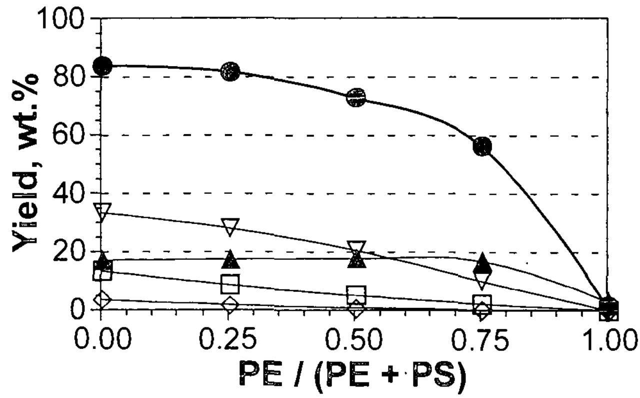
Table 2. Yields of products from PE cracking at 440 °C

Reaction Environment:	**Tetralin**	**n-Decane**	**No Solvent**
wt.% of PE			
Gas	**0.1**	**0.8**	**1.7**
Oil	**0.8**	**1.6**	**53.9**
total C5–C9 n-alkanes	0.0	3.2	6.8
Residue	**99.1**	**97.6**	**44.4**



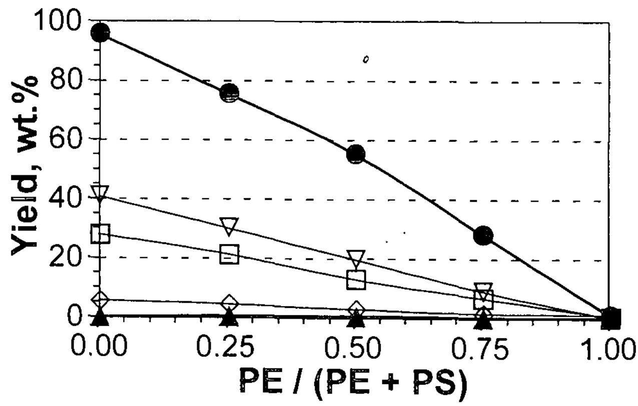
Δcumene □ethylbenzene ∇toluene ▲C5-C9 n-alkanes ●oil

Figure 1. Effect of plastics mixing on yields of products without solvent



Δcumene □ethylbenzene ∇toluene ▲C5-C9 n-alkanes ●oil

Figure 2. Effect of n-decane on yields of products due to PS-PE mixing



Δcumene □ethylbenzene ∇toluene ▲C5-C9 n-alkanes ●oil

Figure 3. Effect of tetralin on yields of products due to PS-PE mixing